



UNIVERSITI PUTRA MALAYSIA

**PREPARATION OF POROUS SILICON BY ELECTROCHEMICAL
ETCHING IN THE FABRICATION OF A SOLAR CELL**

MAGENTHARAU ADIN NARAINA

FSAS 2003 52

**PREPARATION OF POROUS SILICON BY ELECTROCHEMICAL ETCHING
IN THE FABRICATION OF A SOLAR CELL**

By

MAGENTHARAU ADIN NARAINA

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in
Fulfilments of the Requirements for the Degree of Master of Science**

Disember 2003



DEDICATION

TO MY BELOVED FAMILY

Abstract of thesis to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

PREPARATION OF POROUS SILICON BY ELECTROCHEMICAL ETCHING IN THE FABRICATION OF A SOLAR CELL

By
MAGENTHARAU ADIN NARAINA

Disember 2003

Chairman: Associate Professor Mansor Hashim, Ph.D.

Faculty: Science and Environmental Studies

Porous silicon samples have been prepared using electrochemical etching technique. In this project, a 3 cm x 5cm single crystal p-type silicon wafer <422>, resistivity 19.64 Ωcm with thickness of 200 μm was used to prepare porous silicon. The silicon was etched in an aqueous solution at the current density of 5 mA/cm² for 30 minutes under illumination of a 100W halogen lamp at room temperature. The SEM, EDAX and XRD analysis were carried out to exhibit the physical properties of porous silicon. Then the porous silicon was doped with n-type material (Sb) and diffused at temperature of 600°C for 15 minutes to form p-n junction. The prepared sample was deposited with Aluminium at back and front of the sample to form electrical contact. The porous silicon solar cells were measured for efficiency using a sun simulator. From the SEM analysis, the morphology exhibit the island type surface and EDAX analysis which shows oxide layers are mainly incorporated near the surface of porous silicon. The XRD results revealed that the peak had widened and x-ray counts increased. Finally,

an efficiency measurement was conducted to determine the efficiency of the designed porous silicon cell. The highest efficiency percentage achieved for prepared porous silicon cell is 10.5% only compared to current solar cells GaAs which can achieve up to 31.0% percent.

Abstrak tesis dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

**PENGHASILAN POROUS SILIKON MELALUI PUNARAN ELEKTROKIMIA
DALAM PEMBENTUKKAN SEL SOLAR**

Oleh

MAGENTHARAU ADIN NARAINA

Disember 2003

Pengerusi: Profesor Madya Mansor Hashim, Ph.D.

Fakulti: Sains dan Pengajian Alam Sekitar

Silikon berliang disediakan dengan menggunakan teknik punaran kimia. Dalam projek ini, wafer silikon jenis-p hablur tunggal 3cm x 5cm, orientasi <422>, kerintangan $19.64\Omega\text{cm}$ dengan ketebalan $200\mu\text{m}$ digunakan untuk menyediakan silikon berliang. Silikon dipunarkan dalam larutan asid cair pada ketumpatan arus sebanyak $5\text{mA}/\text{cm}^2$ selama 30 minit di bawah sinaran lampu halogen 100W pada suhu bilik. Kajian SEM, EDAX dan XRD dijalankan untuk mengkaji sifat fizik silikon berliang. Silikon berliang didopkan dengan bahan jenis-n (Sb) dan membaur pada suhu 600°C selama 15 minit untuk menghasilkan simpangan p-n. Sampel yang disediakan ini dimendapkan dengan Aluminium di belakang dan depan sel untuk menghasilkan sentuhan elektrik. Kemudian kecekapan sel silikon berliang diukur dengan menggunakan pensimulasi matahari. Daripada analisis SEM, struktur permukaan menunjukkan permukaan bentuk pulau-pulau dan kajian EDAX menunjukkan kewujudan oksida dipermukaan silikon berliang. XRD menunjukkan puncaknya menjadi lebih lebar dan bacaan x-ray meningkat.

Akhirnya, ukuran kecekapan dilakukan ke atas sel yang direka cipta. Kecekapan paling tinggi dicapai adalah hanya 10.5% manakala solar sel GaAs yang ada sekarang telah mencapai kecekapan sehingga 31.0%.

ACKNOWLEDGEMENTS

First of all, thank God, for given me the strength and wisdom to complete my research work. Without god's grace, I wouldn't able to complete my thesis.

I would like to express my sincere gratitude to my supervisor Associate Professor Dr. Mansor Hashim and also co-supervisors, Professor Dr. Abdul Halim Shaari, Professor Dr. Wan Mahmood Mat Yunus and Associate Professor Dr. Zulkarnain Zainal for their precious guidance, encouragement and support.

I am very grateful to my parents and family members and also relatives for their valuable support during my studies. Not forgotten also, my colleagues and friends for their direct and indirect co-operation in this work.

Finally, I am very thankful to Physics Department's Staff (Universiti Putra Malaysia), Texas Instruments (M) Sdn. Bhd. and BP Solar (M) Sdn. Bhd. for their valueable commitment and help in this research.

I certify that an Examination Committee met on 13th November 2003 to conduct the final examination of Magentharau Adin Naraina on his Master of Science thesis entitled “Preparation of Porous Silicon by Electrochemical Etching in the Fabrication of a Solar Cell” in accordance with Universiti Putra Malaysia (Higher Degree) Act 1980 and Universiti Putra Malaysia (Higher Degree) Act 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

AZMI ZAKARIA, PH.D.

Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Chairman)

MANSOR HASHIM, PH.D.

Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

ABDUL HALIM SHAARI, PH.D.

Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

WAN MAHMOOD MAT YUNUS, PH.D.

Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

ZULKARNAIN ZAINAL, PH.D.

Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)



GULAM RUSUL RAHMAT, Ph.D.

Professor / Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 28 Jan 2004

This thesis submitted to the Senate of University Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee are as follows:

MANSOR HASHIM, PH.D.

Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

ABDUL HALIM SHAARI, PH.D.

Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

WAN MAHMOOD MAT YUNUS, PH.D.

Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)

ZULKARNAIN ZAINAL, PH.D.

Associate Professor
Faculty of Science and Environmental Studies
Universiti Putra Malaysia
(Member)



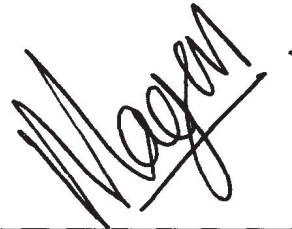
AINI IDERIS, Ph.D.

Professor / Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: **25 FEB 2004**

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledge. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.



MAGENTHARAU ADIN NARAINA

Date: 29 / 01 / 2004

TABLE OF CONTENTS

	Page
DEDICATION	ii
ABSTRACT	iii
ABSTRAK	v
ACKNOWLEDGEMENTS	vii
APPROVAL SHEETS	viii
DECLARATION FORM	x
LIST OF TABLES	xii
LIST OF FIGURES	xiv
LIST OF APPENDICES	xvii
NOMENCLATURES	xviii
 CHAPTER	
 1 INTRODUCTION	
1.1 Introduction	1
1.2 History of Photovoltaics	3
1.3 Objectives and Scope of the Research	5
1.4 Structure of the Thesis	6
 2 LITERATURE REVIEW	
2.1 Porous Silicon	
2.1.1 History of Porous Silicon	8
2.1.2 Formation Mechanism Of Porous Silicon	11
2.1.3 Chemical Mechanisms Determining The Morphology of Porous Silicon	13
2.1.4 Porous Silicon Fabrication Techniques	16
2.1.5 Structure of Porous Silicon	19
2.2 Solar Energy	24
2.3 Solid State	
2.3.1 Materials and Solid State Mechanisms	27
2.3.2 Non-rectifying Ohmic Contacts	34
2.4 Magnetron Sputtering	37
2.5 Photovoltaic Theory	
2.5.1 The Generation of Charge Carriers by The Absorption of Light	38
2.5.2 Recombination, Carrier Lifetime	43
2.5.3 Light Interaction Mechanism in Solar Cell	47
2.5.4 Theory of Photovoltaic (Dember) Effect	49
2.5.5 The Current-Voltage Characteristic of an Illuminated Infinite Solar Cell	53
2.6 Scanning Electron Microscope	57
2.7 X-Ray Diffraction	59



2.7.1	Bragg's Law	60
2.8	Energy Dispersive X-Ray Spectrometry	62
3	METHODOLOGY	
3.1	Introduction	63
3.2	Experimental Technique	63
3.3	p-n Junction Formation	66
3.4	Electrical contact formation	68
3.5	Efficiency Measurements	72
3.6	Sample preparation for SEM and EDAX	74
3.7	XRD Diffraction	77
4	RESULTS AND DISCUSSION	
4.1	Optical and Scanning Electron Microscope	79
4.2	Energy Dispersive X-ray Spectrometry	83
4.2	X Ray Diffraction	92
4.3	Porous Silicon Solar Cell Efficiency	94
5	CONCLUSION AND RECOMMENDATION	
5.1	Conclusion	103
5.2	Future Work for Porous Silicon	105
5.3	Suggestions Solar Cells	106
5.4	Summary	107
	REFERENCES	108
	APPENDICES	111
	VITA	118

LIST OF TABLES

Table		Page
2.1	Equilibrium constants for chemical reactions assisting the PS growth	14
2.2	Value of work function (eV)	36
4.1	Chemical elements in the single point at porous silicon island	80
4.2	Chemical elements in the complete area on porous silicon island	85
4.3	Chemical elements in a crack of porous silicon	86
4.4	Chemical elements in the porous silicon crack and island on the porous silicon	87
4.5	Chemical elements in the complete wide area in the porous silicon	88
4.6	Chemical elements in the complete wide area in the porous silicon	89
4.7	Atomic percentages of elements in the EDAX spectrum	91
4.8	I-V characterization results for pure silicon cell	94
4.9	Porous silicon solar cell data obtained from the graph	99

LIST OF FIGURES

Figure	Page
2.1 Tuner's Chemical Etching Model	17
2.2 Simplified Etching Model	18
2.3 Equipment for anodization in hydrofluoric acid solution	19
2.4 Schematic structure of porous silicon layer	20
2.5 X-ray diffraction of silicon and porous silicon	21
2.6 Texture	22
(a) Pyramid texture model	
(b) Pores texture model	
2.7 (a) Light reflected twice before escape	23
(b) Light is reflected many time in the pores before escape	
2.8 Electron microscopic picture of porous silicon morphology	24
2.9 n-type semiconductor	29
(a) Atomic bond	
(b) Band diagram	
2.10 p-type semiconductor	30
(a) Atomic bond	
(b) Band diagram	
2.11 (a) P and N type Semiconductor Energy Band	31
(b) Joining p and n type semiconductor	
2.12 Bending of Energy Bands, Energy Distribution, Fermi Level and Fermi Potentials at Equilibrium.	32
2.13 Space-Charge Region at the Junction	33
2.14 Electric Field at the Junction	33
2.15 Metal and P-type Semiconductor Ohmic contacts ($\Phi_m > \Phi_s$)	35



2.16	Metal and N-type Semiconductor Ohmic contacts ($\Phi_m < \Phi_s$)	35
2.17	Energy of the conduction band as a function of crystal momentum (Direct semiconductor)	40
2.18	Energy of the conduction band as a function of crystal momentum (Indirect semiconductor)	42
2.19	Radiative recombination (a) in direct semiconductor (b) in indirect semiconductor	44
2.20	Auger combination (a) In The Conduction Band (b) In The Valence Band	45
2.21	Electronic Energy Band Structure at a p-n Junction in Solar Cell	47
2.22	Schematic representation of light interaction and photoelectric current flow	48
2.23	Voltage-Current characteristic of an infinite solar cell	55
2.24	Schematic Scanning Electron Microscope	58
2.25	Bragg's Law	60
3.1	Setup of an electrochemical cell for porous silicon formation	65
3.2	Schematic quartz tube furnace	67
3.3	Furnace for impurity doping	67
3.4	Edward Coating System E306A machine for RF sputtering	69
3.5	Mask for RF magnetron sputtering to deposit metal	70
3.6	Efficiency measurements	72
3.7	SPI-Cell Test 150	74
3.8	Scanning electron microscope	76
3.9	XRD sample holder	77
3.10	Philips x-ray diffraction machine	78

4.1	Weight Losses (%) versus Time (minutes) For Porous Silicon	80
4.2	Optical Microscope Picture With Low Magnification	81
4.3	Optical Microscope Picture With High Magnification	82
4.4	Plan View Scanning Electron Microscope Picture	83
4.5	Morphology Picture for Energy Dispersive X-ray Spectrums	84
4.6	Spectrum of single point on the porous silicon island	85
4.7	Spectrum of complete area on the porous silicon island	86
4.8	Spectrum of a crack on the porous silicon	87
4.9	Spectrum of crack and island together on the porous silicon	88
4.10	Spectrum of complete wide area in the porous silicon	89
4.11	X-Ray Diffraction for silicon and porous silicon	92
4.12	Solar cell I-V characteristics for pure silicon	96
4.13	Solar cell I-V characteristics for porous silicon (sample A)	97
4.14	Solar cell I-V characteristics for porous silicon (sample B)	97
4.15	Solar cell I-V characteristics for porous silicon (sample C)	98
4.16	Solar cell I-V characteristics for porous silicon (sample D)	98
4.17	Solar cell I-V characteristics for porous silicon (sample D)	99
4.18	Porous silicon solar cell efficiency (%) and fill factor versus time	100
4.19	Porous silicon solar open circuit volt (V_{oc}) and short circuit current (I_{sc}) versus time (minutes)	101

APPENDICES

Appendix	Page
Appendix A I-V characterization for pure silicon	111
Appendix B I-V characterization for porous silicon (Sample A)	112
Appendix C I-V characterization for porous silicon (Sample B)	113
Appendix D I-V characterization for porous silicon (Sample C)	114
Appendix E I-V characterization for porous silicon (Sample D)	115
Appendix F I-V characterization for porous silicon (Sample E)	116
Appendix G Standard operating procedure for X-Ray machine	117

NOMENCLATURE

ϕ_{metal}	Metal work function
$\phi_{\text{semiconductor}}$	Semiconductor work function
F_x	Number of photon at point x
$F_{x,0}$	Number of photon on the surface $x = 0$;
α_λ	Absorption coefficient
C	2×10^4 (Direct Semiconductor) when absorption coefficient α in cm^{-1}
E_g	Energy gap of the direct semiconductor
λ	Wavelength of light
λ_p	External energy
h	Planck's constant
c	Speed of light in vacuum
p	Hole concentration
n	Electron concentration
B	Auger coefficient for the material
E_{photon}	Photon's Energy
E_{gap}	Energy Gap
q	electronic charge
μ_n	mobility of electrons
μ_p	mobility of holes
ξ_y	Electric field
k_B	Boltzmann Constant

T	Temperature in Kelvin
η	efficiency of excitation of electron-hole pairs by light absorption
L_n	diffusion length for electrons
I_o	incident light intensity
R	reflection coefficient
τ_n	electron lifetime
s	surface recombination velocity
ν	frequency
U_T	Voltage Generated by Temperature
I_L	Current Generated by Light Incident
I_o	Saturation Current
w	width of the electron beam
M	magnification
W	width of the CRT
d	distance between the two atoms
θ	X-Ray diffraction angle
n	Diffraction order; 1, 2, 3, ...
V_{oc}	Open circuit voltage
V_m	Maximum Voltage
I_m	Maximum Current
P_m	Maximum Power Generated
I_{sc}	Short Circuit Current
R_a	Resistor Load

FF

Fill Factor

CHAPTER 1

INTRODUCTION

1.1 Introduction

In recent years, the use of renewable forms of energy has found increasing recognition as one of the foundations of an ecologically responsible world economy. Of all the renewable energy technologies, photovoltaic (PV) or conversion of light energy to electrical energy shows the greatest promise for worldwide acceptance and application. The sun may be the only energy source big enough to wean off fossil fuels. Their universal appeal lies in the fact that they generate electricity from the sun. A working photovoltaic has no moving parts and it is relatively simple in design, which needs very little maintenance and is environmentally benign. Whenever they are exposed to light, they simply and silently produce electricity. Photovoltaics are solar cells that produce electricity directly from sunlight. It is one of the commercially more mature renewable energy technologies. They are usually made of silicon, the same material that makes up the common beach sand which is used to produce computer chips.

Many remote area uses of photovoltaics are cost-effective and practical now. Photovoltaics generate power for both on-and off-shore traffic control systems, crop irrigations systems, bridge corrosion inhibitors and radio relay stations. They also provide electricity to remote cabins, villages, medical centers and other isolated sites

where the cost of photovoltaics is less than the expense of extending cables from utility power grids or producing diesel-generated electricity.

On the other hand, porous silicon (PS) has many potential applications in displays, sensors, microelectronics, optics, and optoelectronics because of its photoluminescence and related properties. However, certain obstacles have limited the use of PS. Since the discovery of photoluminescence and electroluminescence in porous silicon at room temperature, there has been a great interest in the possibility of producing optoelectronic devices from this material. The discovery of photoluminescence (PL) and electro luminescence (EL) from porous silicon and the understanding of the growth of nanostructures has opened new fields in silicon based optoelectronics and recently solar cell technology.

It was recently found that a diode structure of metal/porous silicon/p-type silicon is light sensitive, allowing the development of porous silicon-based solar cell and photo detectors. Conversions of both light into electricity (solar cells) and electricity into light (EL) of various wavelengths from ultraviolet through to infrared in a quantum system can occur from the absorption or emission of a photon respectively via the formation of an electronic state in many semiconductors.

Porous silicon has certain properties that make it very attractive for photovoltaic applications. Porous silicon has been found to be a good antireflection

(AR) coating for solar cells. Moreover, due to the porous nature of the surface, it can be used to surface morphology texturing of a single or multicrystalline silicon materials. Since Porous silicon has a larger band gap than silicon, it can also act as a surface-passive layer.

Bulk crystalline silicon can be made highly porous by electrochemical etching in HF based electrolyte. When the current density of HF solution is below the critical value, it will etch the surface of the silicon. On the other hand, it is limited to ionic mass transfer, which the electrode surface will be polished or smoothed. The critical value for sample were determine from a top peak in the I-V (current – potential) graph, which plotted using the experiment data. Critical value depends on the temperature, HF concentration and sample's properties.

1.2 History of Photovoltaic

In 1839 Edmund Becquerel, the French experimental physicist, discovered the photovoltaic effect while experimenting with an electrolytic cell made up of two metal electrodes placed in an electricity-conducting solution which current generation increased when exposed to light.

Willoughby Smith discovered the photoconductivity of selenium in 1873. This followed by W.G. Adams and R.E. Day made first selenium photovoltaic in 1877. Hertz discovered that ultraviolet light altered the lowest voltage capable of causing a spark to jump between two metal electrodes in 1887

In 1921, Photoelectric effect theory was explained by Albert Einstein, which he won a Nobel Prize. U.S. Signal Corps assigned the task of providing power supplies for the first U.S. Earth satellites in 1955, which have 2% efficiency. Western Electric began to sell commercial licenses for silicon PV technologies. Early successful products included PV-powered dollar bill changers and devices that decoded computer punch cards and tape. Then, the photovoltaic technology proposed for orbiting Earth satellites. In 1960, Hoffman Electronics achieves 14-percent efficient PV cells using selenium and silicon material. The first Orbiting Astronomical Observatory launched with a photovoltaic array of 1kW in 1966.

From 1976 through 1985 and from 1992 to 1995, the NASA Lewis Research Center (LeRC) project office installed 83 photovoltaics power systems on every continent except Australia. These systems provide the operational energy for such diverse applications as vaccine refrigeration, room lighting, medical clinic lighting, telecommunications, water pumping, grain milling, and classroom television. ARCO Solar was the first company to produce more than 1MW of PV modules in one year in early 1980.